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Modelling the fate of ciprofloxacin in activated sludge systems – The relevance of the sorption process

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The sorption process can impact the removal of specific pharmaceuticals in municipal wastewater treatment plants (WWTPs). Ionic interactions (e.g., pH-driven equilibria and complexation), rather than hydrophobic interactions, are known to affect the sorption of zwitterionic pharmaceuticals. In a previous study [1], a daily systematic reduction of ciprofloxacin removal in a full-scale WWTP (Bekkelaget, Norway) was associated to deteriorated sorption. Therefore, in this study we further investigated the sorption of ciprofloxacin onto activated sludge at laboratory- and full-scale. Targeted batch experiments were performed to estimate sorption model parameters using Freundlich isotherms under specific pH and iron salt dosing (used for chemical phosphorus removal) conditions. We used the previously tested activated sludge framework model for xenobiotic trace chemicals (ASM-X) to assess the fate of ciprofloxacin in a full-scale activated sludge system. Sorption was described by linear kinetics and, in an extended version of ASM-X, using a Freundlich-based submodel. In the latter case, Freundlich parameter values estimated from the batch experiments were used for model calibration. The prediction accuracy was statistically evaluated in the two cases by comparing the model output with measured data.

Batch experiments showed that maximum sorption capacity occurred at pH=7.4, corresponding to the isoelectric point of ciprofloxacin. A pH increase resulted in a significant reduction of sorption capacity as compared to the effect of the pH decrease applied in the experiment. Additionally, iron salt dosing was found to enhance sorption under both aerobic and anoxic conditions. Using the extended ASM-X model, results obtained in scenario simulations – based on the batch experimental Freundlich parameters – suggest that pH conditions, rather than reduced salt dosing, can be responsible for the decrease of ciprofloxacin sorption in the full-scale WWTP. The most accurate predictions were obtained for Freundlich parameter values of K=0.01 ($\mu g^{(1-1/n)}$ $L^{1/n}$ mg^{-1}) and 1/n=1.33. A pH increase was therefore estimated to cause reduced sorption in the anoxic and the aerobic reactors, possibly being a consequence of the lower sorption extent exhibited by the anionic ciprofloxacin species. Comparable prediction accuracy was obtained using linear sorption. A 20-fold decrease of the anoxic and aerobic K_D values (1.1 and 0.42 L gX_{SS}^{-1} under normal conditions, respectively) was estimated in the time interval when deteriorated sorption was hypothesized.

[1] Plósz, B.G.; Leknes, H.; Thomas, K.V. (2010a). *Impacts of competitive inhibition, parent compound formation and partitioning behaviour on antibiotic micro-pollutants removal in activated sludge*. Environmental Science & Technology, 44 (2), 734–742.